

PATENT  
Attorney Docket No. 11610US02IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

#7

## PATENT APPLICATION OF:

CHARLES STONE and  
ALFRED E. STECK

SERIAL NO. 09/503,760

FILED: February 14, 2000

FOR: GRAFT POLYMERIC  
MEMBRANES AND ION-  
EXCHANGE MEMBRANES  
FORMED THEREFROM

GROUP ART UNIT: 1745

EXAMINER: Not yet assigned

## CERTIFICATE OF MAILING

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MAIL ROOMINFORMATION DISCLOSURE STATEMENTAssistant Commissioner for Patents  
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Dear Sir:

Applicants submit herewith a copy of the following  
reference for consideration with the above application.

<u>U.S. Patent No.</u>	<u>Inventor(s)</u>	<u>Issue Date</u>
4,012,303	D'Agostino et al.	03/77
4,420,612	Aiba et al.	12/83
4,506,035	Barnett et al.	03/85
4,605,685	Momose et al.	08/86

<u>U.S. Patent No.</u>	<u>Inventor(s)</u>	<u>Issue Date</u>
5,422,411	Wei et al.	06/95
5,498,639	Wei et al.	03/96
5,602,185	Stone et al.	08/97
5,656,386	Scherer et al.	08/97
5,684,192	Stone et al.	11/97
5,817,718	Nezu et al.	10/98
5,830,962	Feiring et al.	11/98

<u>Foreign Patent No.</u>	<u>Country</u>	<u>Date</u>
0 140 544	EP	05/85
WO 95/08581	PCT	03/95
WO 96/40798	PCT	12/96
WO 97/25369	PCT	07/97

<u>Publication</u>	<u>Author(s)</u>	<u>Date</u>
"Kinetics of Diffusion-Free Radiation Graft Polymerization of Styrene onto Polyethylene", <u>Journal of Polymer Science: Polymer Chemistry Edition</u> , Vol. 15, pp. 469-88.	Babie et al.	1977
"Study of Energy Transfer to Solvent in Radiation Graft Polymerization of Styrene onto Polyethylene", <u>Journal of Polymer Science: Polymer Chemistry Edition</u> , Vol. 15, pp. 1619-28.	Babie et al.	1977

"Radiation Grafting of  $\alpha,\beta,\beta$ -Trifluorostyrene onto Various Polymer Films by Preirradiation Method", Journal of Applied Polymer Science, Vol. 37, pp. 2165-68. Momose et al. 1989

"Radiation Grafting of  $\alpha,\beta,\beta$ -Trifluorostyrene onto Poly(Ethylene-Tetrafluoroethylene) Film By Preirradiation Method. I. Effects of Preirradiation Dose Monomer Concentration, Reaction Temperature, and Film Thickness", Journal of Applied Polymer Science, Vol. 37, pp. 2817-26. Momose et al. 1989

"Radiation Grafting of  $\alpha,\beta,\beta$ -Trifluorostyrene onto Poly(Ethylene-Tetrafluoroethylene) Film By Preirradiation Method. II. Properties of Cation-Exchange Membrane Obtained by Sulfonation and Hydrolysis of the Grafted Film" Journal of Applied Polymer Science, Vol. 38, pp. 2091-101. Momose et al. 1989

"Radiation Grafting of  $\alpha,\beta,\beta$ -Trifluorostyrene onto Poly(Ethylene-Tetrafluoroethylene) Film By Preirradiation Method. III. Properties of Anion-Exchange Membrane Obtained by Chloromethylation and Momose et al. 1989

Quaternization of the Grafted Film", Journal of Applied Polymer Science, Vol. 39, pp. 1221-30.

"Radiation Grafted Membranes: Some Structural Investigations In Relation to Their Behavior in Ion-Exchange Membrane Water Electrolysis Cells", Int. J. Hydrogen Energy, Vol. 17, No. 2, pp. 115-23. Scherer et al. 1992

"Analysis of radiation-grafted membranes for fuel cell electrolytes", J. Applied Electrochem., Vol. 22, pp. 204-14. Guzman-Garcia et al. 1992

"Proton exchange membranes prepared by simultaneous radiation of styrene onto Teflon-FEP films. Synthesis and Characterization", J. Membrane Sci., 81, pp. 89-95. Rouilly et al. 1993

"Cation Exchange Membranes by Pre-Irradiation Grafting Of Styrene onto FEP Films. I. Influence of Synthesis Conditions", J. Polymer Sci.: Part A: Polymer Chemistry, Vol. 32, pp. 1931-37. Gupta et al. 1994

"Proton-Exchange Membranes by Radiation Grafting of Styrene onto FEP Films. II. Mechanism Of Thermal Degradation in Copolymer Membranes", Gupta et al. 1994

J. Applied Polymer  
Sci., Vol. 51, pp.  
1659-66.

The above references are listed on the enclosed Form PTO-1449 entitled "Information Disclosure Citation."

Concise Explanation of The  
Relevance of the Cited Reference

D'Agostino et al. U.S. Patent No. 4,012,303 discloses fluorocarbon polymers and polymeric membranes produced by radiation grafting. For example,  $\alpha,\beta,\beta$ -trifluorostyrene in an inert solvent is grafted onto an inert film, such as tetrafluoroethylene-hexafluoropropylene copolymer, by irradiation. The grafted film is then sulfonated to produce a film useful as a membrane in various electrochemical cells.

Aiba et al. U.S. Patent No. 4,420,612 discloses a catalyst membrane including a porous tetrafluoroethylene membrane having grafted thereon polystyrenesulfonic acid. The catalyst membrane is stated to be useful for hydrocatalyzing water soluble organic substances such as polysaccharides.

Barnett et al. U.S. 4,506,035 discloses microporous hydrophilic fluoropolymer membranes comprising a fluorine-containing substrate to which has been radiation cografted a mixture of monomers. The membranes have enhanced wettability for improved performance in choler-alkali cells.

Momose et al. U.S. Patent No. 4,605,685 discloses a method for preparing graft polymeric membranes comprising an inactive polymer film having trifluorostyrene (TFS) as a graft chain. The inactive polymer is irradiated with ionizing radiation, and the resulting irradiated film is graft-polymerized by contacting the film with TFS. The product may then be sulfonated to provide a cation exchange membrane or haloalkylated and quaternary aminated to provide an anion exchange membrane.

Wei et al. U.S. Patent No. 5,422,411 discloses polymeric compositions derived from copolymers of  $\alpha,\beta,\beta$ -trifluorostyrene with a variety of substituted  $\alpha,\beta,\beta$ -trifluorostyrenes. The compositions are suitable for use as membranes, particularly as ion-exchange membranes, and most particularly as solid polymer electrolytes in electrochemical applications such as, for example, electrochemical fuel cells.

Wei et al. U.S. Patent No. 5,498,639 is a continuation of the Wei U.S. Patent No. 5,422,411.

Stone et al. U.S. Patent No. 5,602,185 is a continuation-in-part of the Wei '411 patent and discloses sulfonyl fluoride substituted  $\alpha,\beta,\beta$ -trifluorostyrene monomers and polymeric compositions incorporating the monomers. The polymeric

compositions are conveniently hydrolyzed to produce polymeric compositions which include ion-exchange moieties. The resulting compositions which include ion-exchange moieties are particularly suitable for use as solid polymer electrolytes in electrochemical applications such as, for example, electrochemical fuel cells.

Scherer et al. U.S. Patent No. 5,656,386 discloses an electrochemical cell having a membrane electrolyte made of a hydrophilic, proton-conducting polymer material. The membrane material is a base polymer that is radiation-grafted with terminally sulfonated vinyl radicals.

Stone et al. U.S. Patent No. 5,684,192 is a division of the Stone '185 patent.

Nezu et al. U.S. Patent No. 5,817,718 discloses a solid-polymer electrolyte membrane for fuel cell and process for producing the same, which is formed of a synthetic resin which comprises of a main chain and a hydrocarbon based side chain. The main chain is formed of a copolymer made from fluorocarbon-based and hydrocarbon based-vinyl monomer. The hydrocarbon-based side chain involves a sulfonic group which is a component for introducing an ion-exchange function into the present solid-polymer electrolyte membrane.

Feiring et al. U.S. Patent No. 5,830,962 discloses partially fluorinated copolymers containing sulfonic acid or sulfonate salt groups and processes for making such copolymers. The copolymers are suited for use as ion-exchange resins and acid catalysts.

European Publication No. 0 140 544 was cited in an International Search Report (copy enclosed herewith) for the PCT/International Application No. PCT/CA98/01041, which corresponds to U.S. Patent Application Serial No. 08/967,960 filed November 12, 1997, of which the present application is a continuation-in-part.

PCT Publication No. WO 95/08581 was cited in an International Search Report (copy enclosed herewith) for the PCT/International Application No. PCT/CA98/01041, which corresponds to U.S. Patent Application Serial No. 08/967,960 filed November 12, 1997, of which the present application is a continuation-in-part.

PCT Publication No. WO 96/40798 discloses polymeric compositions derived from copolymers of substituted and unsubstituted  $\alpha,\beta,\beta$ -trifluorostyrene with a variety of substituted ethylene monomers. The compositions are suitable for use as membranes, particularly as ion-exchange membranes, and more particularly as solid polymer electrolytes in



electrochemical applications such as, for example, electrochemical fuel cells.

PCT Publication No. WO 97/25369 discloses composite membranes in which a porous substrate is impregnated with a polymeric composition comprising various combinations of  $\alpha,\beta,\beta$ -trifluorostyrene, substituted  $\alpha,\beta,\beta$ -trifluorostyrene and ethylene-based monomeric units. Where the polymeric composition includes ion-exchange moieties, the resultant composite membranes are useful in electrochemical applications, particularly as membrane electrolytes in electrochemical fuel cells.

The 1977 publication by Babie et al entitled "Kinetics of Diffusion-Free Radiation Graft Polymerization of Styrene onto Polyethylene" discloses the dependence of radiation-initiated graft polymerization on monomer concentration for the polyethylene-styrene system.

The 1977 publication by Babie et al. entitled "Study of Energy Transfer to Solvent in Radiation Graft Polymerization of Styrene onto Polyethylene" discloses that energy transfer to diluent is not responsible for the previously observed high orders of dependence of the grafting rate on monomer concentration in the radiation initiated graft polymerization of styrene onto polyethylene.

The 1989 publication by Momose et al. entitled "Radiation Grafting of  $\alpha,\beta,\beta$ -trifluorostyrene onto Various Polymer Films by Preirradiation Method" discloses the radiation grafting of TFS onto various polymer films, including fluorine-containing polymers, by preirradiation.

The 1989 publication by Momose et al. entitled "Radiation Grafting of  $\alpha,\beta,\beta$ -Trifluorostyrene onto Poly(Ethylene-Tetrafluoroethylene) Film By Preirradiation Method. I. Effects of Preirradiation Dose, Monomer Concentration, Reaction Temperature, And Film Thickness" discloses pre-irradiation grafting of TFS onto poly(ethylene-tetrafluoroethylene) film. The grafting rate dependency on preirradiation dose, monomer concentration and reaction temperature was calculated. The grafting rate was found to be independent of the film thickness.

The 1989 publication by Momose et al. entitled "Radiation Grafting of  $\alpha,\beta,\beta$ -Trifluorostyrene onto Poly(Ethylene-Tetrafluoroethylene) Film by Preirradiation Method. II. Properties of Cation-Exchange Membrane Obtained by Sulfonation and Hydrolysis of the Grafted Film" discloses the determination of swelling, water uptake, electric conductivity, and transport number of cation exchange membranes obtained by the

preirradiation grafting of TFS onto poly(ethylene-tetrafluoroethylene), followed by sulfonation and hydrolysis of the grafted film.

The 1989 publication by Momose et al. entitled "Radiation Grafting of  $\alpha,\beta,\beta$ -Trifluorostyrene onto Poly(Ethylene-Tetrafluoroethylene) Film by Preirradiation Method. III. Properties of Anion-Exchange Membrane Obtained by Chloromethylation and Quaternization of the Grafted Film" discloses the determination of swelling, water uptake, electric conductivity, and transport number of anion exchange membranes obtained by the preirradiation grafting of TFS onto poly(ethylene-tetrafluoroethylene), followed by chloromethylation and quaternization of the grafted film.

The 1992 publication by Scherer et al. entitled "Radiation Grafted Membranes: Some Structural Investigations In Relation to Their Behavior in Ion-Exchange Membrane Water Electrolysis Cells" discloses structural investigation of three radiation grafted cation exchange membranes.

The 1992 publication by Guzman-Garcia entitled "Analysis of radiation-grafted membranes for fuel cell electrolytes" discloses radiation grafted copolymer membranes containing poly(styrenesulphonic acid) side chains and three different backbone polymer structures; low-density polystyrene,

polytetrafluoroethylene/poly(perfluoropropylene), and polytetrafluoroethylene.

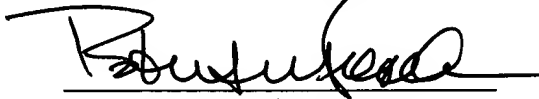
The 1993 publication by Rouilly et al. entitled "Proton exchange membranes prepared by simultaneous radiation of styrene onto films onto Teflon-FEP films. Synthesis and characterization" discloses the simultaneous radiation grafting of styrene onto Teflon-FEP (polytetrafluoroethylene and a copolymer of tetrafluoroethylene and hexafluoropropylene) films and subsequent sulfonation.

The 1994 publication by Gupta et al. entitled "Cation Exchange Membranes by Pre-Irradiation Grafting of Styrene onto FEP Films. I. Influence of Synthesis Conditions" discloses gamma radiation-induced grafting of styrene into FEP films.

The 1994 publication by Gupta entitled "Proton-Exchange Membranes by Radiation Grafting of Styrene onto FEP Films. II. Mechanism of Thermal Degradation in Copolymer Membranes" discloses the thermal degradation of radiation-grafted and sulfonated FEP-g-polystyrene membrane.

Please charge any fees incurred in connection with this submission to Deposit Account No. 13-0017 in the name of McAndrews, Held & Malloy, Ltd.

Respectfully submitted,



Robert W. Fieseler  
Registration No. 31,826  
Attorney for Applicants

McANDREWS, HELD & MALLOY, LTD.  
500 West Madison Street, 34th Floor  
Chicago, Illinois 60661

Telephone: (312) 775-8000  
Facsimile: (312) 775-8100

Dated: June 6, 2000